

## PCT COOPERATION TREATY

PCT

NOTIFICATION OF THE RECORDING  
OF A CHANGE(PCT Rule 92bis.1 and  
Administrative Instructions, Section 422)

From the INTERNATIONAL BUREAU

To:

DE BRUIJN, Leendert, C.  
Nederlandsch Octrooibureau  
Scheveningseweg 82  
P.O. Box 29720  
NL-2502 LS The Hague  
PAYS-BAS

<b>Date of mailing</b> (day/month/year) 12 April 2001 (12.04.01)	<b>IMPORTANT NOTIFICATION</b>
<b>Applicant's or agent's file reference</b> BO 41866	
<b>International application No.</b> PCT/NL99/00624	<b>International filing date</b> (day/month/year) 08 October 1999 (08.10.99)

## 1. The following indications appeared on record concerning:

☒ the applicant
 ☒ the inventor
 ☐ the agent
 ☐ the common representative

<b>Name and Address</b> JANSSEN, Arnoldus, Hermanus, Henderikus G.A. Holzmüller-Teengsstraat 3 NL-1827 PJ Alkmaar Netherlands	<b>State of Nationality</b> NL	<b>State of Residence</b> NL
	<b>Telephone No.</b>	
	<b>Facsimile No.</b>	
	<b>Teleprinter No.</b>	

## 2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

☐ the person
 ☒ the name
 ☐ the address
 ☐ the nationality
 ☐ the residence

<b>Name and Address</b> JANSSEN, Arnoldus, Hermannus, Henderikus G.A. Holzmüller-Teengsstraat 3 NL-1827 PJ Alkmaar Netherlands	<b>State of Nationality</b> NL	<b>State of Residence</b> NL
	<b>Telephone No.</b>	
	<b>Facsimile No.</b>	
	<b>Teleprinter No.</b>	

## 3. Further observations, if necessary:

## 4. A copy of this notification has been sent to:

<input checked="" type="checkbox"/> the receiving Office	<input type="checkbox"/> the designated Offices concerned
<input type="checkbox"/> the International Searching Authority	<input checked="" type="checkbox"/> the elected Offices concerned
<input checked="" type="checkbox"/> the International Preliminary Examining Authority	<input type="checkbox"/> other:

<b>The International Bureau of WIPO</b> 34, chemin des Colombettes 1211 Geneva 20, Switzerland  Facsimile No.: (41-22) 740.14.35	<b>Authorized officer</b>  Maria Victoria CORTIELLO  Telephone No.: (41-22) 338.83.38
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## PATENT COOPERATION TREATY

PCT

## NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents  
United States Patent and Trademark  
Office  
Box PCT  
Washington, D.C.20231  
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

<b>Date of mailing</b> (day/month/year) 03 May 2000 (03.05.00)	
<b>International application No.</b> PCT/NL99/00624	<b>Applicant's or agent's file reference</b> BO 41866
<b>International filing date</b> (day/month/year) 08 October 1999 (08.10.99)	<b>Priority date</b> (day/month/year) 08 October 1998 (08.10.98)
<b>Applicant</b> MAKKUS, Robert, Christiaan et al	

1. The designated Office is hereby notified of its election made:

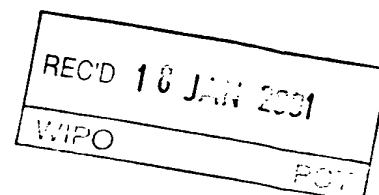
☒ in the demand filed with the International Preliminary Examining Authority on:

20 March 2000 (20.03.00)

☐ in a notice effecting later election filed with the International Bureau on:
2. The election ☒ was
☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

<b>The International Bureau of WIPO</b> 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	<b>Authorized officer</b> Claudio Borton Telephone No.: (41-22) 338.83.38
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## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference BO 41866	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/NL99/00624	International filing date (day/month/year) 08/10/1999	Priority date (day/month/year) 08/10/1998
International Patent Classification (IPC) or national classification and IPC H01M8/02		
Applicant STICHTING ENERGIEONDERZOEK CENTRUM NEDERLAND et al		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.



2. This REPORT consists of a total of 6 sheets, including this cover sheet.

- ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 1 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand  20/03/2000	Date of completion of this report  16.01.2001
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer  Thanos, I  Telephone No. +49 89 2399 8462 

# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/NL99/00624

## I. Basis of the report

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).):*

### Description, pages:

1-3 as originally filed

### Claims, No.:

2-5,7-9 as originally filed

1,6 as received on 22/06/2000 with letter of 21/06/2000

### Drawings, sheets:

1/2,2/2 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
  - ☐ the language of publication of the international application (under Rule 48.3(b)).
  - ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).
3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:
- ☐ contained in the international application in written form.
  - ☐ filed together with the international application in computer readable form.
  - ☐ furnished subsequently to this Authority in written form.
  - ☐ furnished subsequently to this Authority in computer readable form.
  - ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
  - ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.
4. The amendments have resulted in the cancellation of:

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/NL99/00624

- ☐ the description,      pages:  
☐ the claims,      Nos.:  
☐ the drawings,      sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

1. Statement

Novelty (N)	Yes: Claims 2-9
	No: Claims 1
Inventive step (IS)	Yes: Claims 6-9
	No: Claims 1-5
Industrial applicability (IA)	Yes: Claims 1-9
	No: Claims

2. Citations and explanations  
**see separate sheet**

**VIII. Certain observations on the international application**

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:  
**see separate sheet**

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

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International application No. PCT/NL99/00624

Re PART V:

Citations:

D1 = JP-A-5339748, assessed in particular on the basis of its WPI-abstract in English  
D2 = WO-A-96/35825

Explanations:

1. WPI-abstract of document D1 refers to a method of coating a carbon steel substrate with ceramic layer comprising 13% TiO<sub>2</sub>, followed by electrocoating a Ni layer. The fact that electrodeposition was possible in the process described in D1 is an indication of the **electroconductivity** of the coated carbon steel. Present claim 1 does not rule out the possibility of forming further coatings on top of the Ni-layer. Thus, the subject-matter of claim 1 is considered to lack novelty vis-à-vis the teaching of document D1 (Art. 33(2)). The method of claim 1 concerns the fabrication of coated steel not required to be particularly adapted to be used in a particular technical application. Thus, from this point of view trivial modifications of the method of claim 1 to establish novelty would not necessarily give rise to inventive subject-matter (Art. 33(3), PCT).
  - 1.1 The applicant argued in an intermediate response that the presence of pinholes in the titanium oxide-comprising (under)coating disposed between the steel plate and the nickel coating does not lend itself with diffusion barrier properties. Nevertheless, the wording of present claim 1 does not embrace exclusively pinhole-free undercoatings. Apart of not specifying in claim 1 that the said undercoating is the layer endowed with diffusion barrier properties (in some cases the nickel layer which is pinhole-free may function as a diffusion barrier) the wording of said claim requires a step "comprising applying a diffusion barrier", i.e. that at least portions of a coating are comprised which may act as a diffusion barrier (the pinhole-free portions are such portions). Thus, in whatever way claim 1 is construed, novelty over the teaching of document D1 is not ensured.
2. Optimising the thickness of a functional coating and the formation of adhesion-improving pre-coatings on a given (steel) substrate concern process steps to be

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/NL99/00624

rated as routine-like ones; NiCrAlY is a well-known alloy used to interconnect metallic and ceramic films on substrates intended to be used in high temperature applications. Thus, the subject-matters of claims 2-5 are not considered to involve an inventive step (Art. 33(3), PCT).

3. Claim 6, directed to a fuel cell comprising a stainless steel separator coated with an intermediate layer comprising TiO<sub>2</sub> and overcoated with a "Ni layer" (generally interpreted as a layer comprising Ni, even if in the description the respective layer is always described as one consisting of Ni), specifies that a layer of **TiO<sub>2</sub>** (preferably 25 micrometer thick or more) **is present** in the "layer comprising TiO<sub>2</sub>" **already prior to any use of the coated "stainless steel support"**, e.g. as a fuel cell separator.
- 3.1 It is known that other Ti-ceramic films (e.g. made of titanium nitride) described in analogous prior art embodiments are oxidised during use to produce TiO<sub>2</sub> with undesired physical properties (cf. description page 1, lines 23-26). As a matter of fact, a stainless steel support coated at first with a TiN-layer and subsequently with a "Ni layer" is bound to comprise TiO<sub>2</sub> obtained by in-situ oxidation of titanium nitride during use as a separator in high temperature fuel cell stacks (as described in D2, Example 4 at page 5, lines 4-18, read in conjunction with the explanations set forth at page 3, lines 7-9).
- 3.2 Even so, a fuel cell stack as assembled prior to its use may be distinguished from a respective fuel cell stack according to document D2, since a separator plate thereof comprises titanium already prior to any use (Art. 33(2), PCT). This kind of separators are partly converted into a Li<sub>2</sub>TiO<sub>3</sub> and are particularly adapted to suppress corrosion in carbonate fuel cells. Instead, the separators proposed in D2 are particularly adapted for use in solid electrolyte high temperature cells. Hence, the subject-matter of claim 6 and those of dependent claims 7-9 are considered to involve both novelty and inventive step (Art. 33(2),(3), PCT); see however remarks put forward under PART VIII.

Re PART VIII:

Claim 6 does not clarify that its wording embraces only fuel cell stacks including

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

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International application No. PCT/NL99/00624

unused separators (Art. 6). To the extent, that already used fuel cells comprising separators of the aforestated design are embraced by the wording of claim 6, the subject-matter of that claim would be considered to lack even novelty in the light of the remarks set forth under points 3 and 3.1 above.



22.06.2000

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(59)

**Claims**

5 1. Method for coating a non-oxidised stainless steel support plate with an electrically conducting corrosion-resistant coating, comprising applying a diffusion barrier layer containing a titanium compound, followed by applying a nickel layer, characterised in that applying said diffusion barrier layer comprises the application of a titanium oxide containing compound before applying said nickel layer.

10 6. Fuel cell stack comprising a number of cells each having a cathode, anode and electrolyte, wherein said cells are separated by a separator plate, said separator plate comprising a support plate of stainless steel coated on the anode side with a diffusion barrier layer comprising titanium oxide provided with a nickel layer, said diffusion layer comprising titanium oxide being provided before the application of said nickel layer.

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A.D

## PATENT COOPERATION TREATY

## PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>BO 41866</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. <b>PCT/NL 99/00624</b>	International filing date (day/month/year) <b>08/10/1999</b>	(Earliest) Priority Date (day/month/year) <b>08/10/1998</b>
Applicant <b>STICHTING ENERGIEONDERZOEK CENTRUM NEDERLAND et al</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.



It is also accompanied by a copy of each prior art document cited in this report.

**1. Basis of the report**

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.



the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing:



contained in the international application in written form.



filed together with the international application in computer readable form.



furnished subsequently to this Authority in written form.



furnished subsequently to this Authority in computer readable form.



the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.



the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,



the text is approved as submitted by the applicant.



the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,



the text is approved as submitted by the applicant.



the text has been established, according to Rule 38, by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure



as suggested by the applicant.



because the applicant failed to suggest a figure.



because this figure better characterizes the invention.



None of the figures.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 99/00624

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H01M8/02 C23C28/00 C23C4/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01M C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 686 706 A (CITIZEN WATCH CO LTD) 13 December 1995 (1995-12-13) claims 1,11; example 4 ---	1
A	DATABASE WPI Section Ch, Week 9404 Derwent Publications Ltd., London, GB; Class F09, AN 94-032177 XP002105853 & JP 05 339748 A (MITSUBISHI HEAVY IND CO LTD), 21 December 1993 (1993-12-21) abstract ---	1
A	DE 195 23 637 A (MOTOREN TURBINEN UNION) 4 July 1996 (1996-07-04) cited in the application claims 1,8,14,15,3617 --- -/--	1,6



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

### Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

11 January 2000

Date of mailing of the international search report

20/01/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.  
Fax: (+31-70) 340-3016

Authorized officer

D'hondt, J

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/NL 99/00624

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 96 35825 A (TANNENBERGER HELMUT) 14 November 1996 (1996-11-14) page 3, paragraph 2; claims 1,4,8,10 ----	1
A	PATENT ABSTRACTS OF JAPAN vol. 013, no. 302 (C-616), 12 July 1989 (1989-07-12) & JP 01 092350 A (OSAKA GAS CO LTD), 11 April 1989 (1989-04-11) abstract -----	
A	DE 26 19 417 A (OTT WALTER H R) 24 November 1977 (1977-11-24) -----	

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/NL 99/00624

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0686706 A	13-12-1995	DE 69419310 D DE 69419310 T CN 1116434 A WO 9518248 A US 5985469 A	05-08-1999 16-12-1999 07-02-1996 06-07-1995 16-11-1999
JP 5339748 A	21-12-1993	NONE	
DE 19523637 A	04-07-1996	NONE	
WO 9635825 A	14-11-1996	NONE	
JP 01092350 A	11-04-1989	NONE	
DE 2619417 A	24-11-1977	NONE	

PCT

28.10.99

## REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only

PCT/NL		99/00624
International Application No.		
08 OCT 1999		(08.10.99)
International Filing Date		
BUREAU VOOR DE INDUSTRIËLE EIGENDOM P.C.T. INTERNATIONAL APPLICATION		
Name of receiving Office and "PCT International Application"		
Applicant's or agent's file reference (if desired) (12 characters maximum)		BO 41866

<b>Box No. I TITLE OF INVENTION</b>		Method for coating a support plate and fuel cell provided with such a support plate	
<b>Box No. II APPLICANT</b>			
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)  Stichting Energieonderzoek Centrum Nederland Westerduinweg 3 NL-1755 LE PETTEN The Netherlands		<input type="checkbox"/> This person is also inventor.  Telephone No.  Facsimile No.  Teleprinter No.	
State (that is, country) of nationality: The Netherlands (NL)		State (that is, country) of residence: The Netherlands (NL)	
This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input checked="" type="checkbox"/> all designated States except the United States of America <input type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box			
<b>Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)</b>			
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)  Gemeenschappelijk Centrum voor Onderzoek Petten Postbus 1 NL-1755 ZG PETTEN The Netherlands		This person is: <input checked="" type="checkbox"/> applicant only <input type="checkbox"/> applicant and inventor <input type="checkbox"/> inventor only (If this check-box is marked, do not fill in below.)	
State (that is, country) of nationality: The Netherlands (NL)		State (that is, country) of residence: The Netherlands (NL)	
This person is applicant for the purposes of: <input type="checkbox"/> all designated States <input checked="" type="checkbox"/> all designated States except the United States of America <input type="checkbox"/> the United States of America only <input type="checkbox"/> the States indicated in the Supplemental Box			
<input checked="" type="checkbox"/> Further applicants and/or (further) inventors are indicated on a continuation sheet.			
<b>Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE</b>			
The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:		<input checked="" type="checkbox"/> agent <input type="checkbox"/> common representative	
Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)  DE BRUIJN, Leendert C. [et al] Nederlandsch Octrooibureau Scheveningseweg 82, P.O. Box 29720 NL-2502 LS The Hague THE NETHERLANDS		Telephone No. 70 3527500  Facsimile No. 70 3527528  Teleprinter No.	
<input type="checkbox"/> Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.			

A 20/NL

<b>Continuation of Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)</b>			
<i>If none of the following sub-boxes is used, this sheet should not be included in the request.</i>			
<p><b>Name and address:</b> <i>(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)</i></p> <p>MAKKUS, Robert Christiaan Karekietstraat 8 NL-1826 JM ALKMAAR The Netherlands</p>		<p><b>This person is:</b></p> <p><input type="checkbox"/> applicant only</p> <p><input checked="" type="checkbox"/> applicant and inventor</p> <p><input type="checkbox"/> inventor only <i>(If this check-box is marked, do not fill in below.)</i></p>	
<p><b>State (that is, country) of nationality:</b> The Netherlands (NL)</p>		<p><b>State (that is, country) of residence:</b> The Netherlands (NL)</p>	
<p><b>This person is applicant for the purposes of:</b></p> <p><input type="checkbox"/> all designated States    <input type="checkbox"/> all designated States except the United States of America    <input checked="" type="checkbox"/> the United States of America only    <input type="checkbox"/> the States indicated in the Supplemental Box</p>			
<p><b>Name and address:</b> <i>(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)</i></p> <p>BULLOCK, Edward Eikenlaan 16 NL-1861 GV BERGEN The Netherlands</p>		<p><b>This person is:</b></p> <p><input type="checkbox"/> applicant only</p> <p><input checked="" type="checkbox"/> applicant and inventor</p> <p><input type="checkbox"/> inventor only <i>(If this check-box is marked, do not fill in below.)</i></p>	
<p><b>State (that is, country) of nationality:</b> United Kingdom (GB)</p>		<p><b>State (that is, country) of residence:</b> The Netherlands (NL)</p>	
<p><b>This person is applicant for the purposes of:</b></p> <p><input type="checkbox"/> all designated States    <input type="checkbox"/> all designated States except the United States of America    <input checked="" type="checkbox"/> the United States of America only    <input type="checkbox"/> the States indicated in the Supplemental Box</p>			
<p><b>Name and address:</b> <i>(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)</i></p> <p>JANSSEN, Arnoldus Hermanus Henderikus G.A. Holzmüller-Teengsstraat 3 NL-1827 PJ ALKMAAR The Netherlands</p>		<p><b>This person is:</b></p> <p><input type="checkbox"/> applicant only</p> <p><input checked="" type="checkbox"/> applicant and inventor</p> <p><input type="checkbox"/> inventor only <i>(If this check-box is marked, do not fill in below.)</i></p>	
<p><b>State (that is, country) of nationality:</b> The Netherlands (NL)</p>		<p><b>State (that is, country) of residence:</b> The Netherlands (NL)</p>	
<p><b>This person is applicant for the purposes of:</b></p> <p><input type="checkbox"/> all designated States    <input type="checkbox"/> all designated States except the United States of America    <input checked="" type="checkbox"/> the United States of America only    <input type="checkbox"/> the States indicated in the Supplemental Box</p>			
<p><b>Name and address:</b> <i>(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)</i></p> <p>CASSIR, Michel 4, Rue Edmond Gondinet FR-75013 PARIS France</p>		<p><b>This person is:</b></p> <p><input type="checkbox"/> applicant only</p> <p><input checked="" type="checkbox"/> applicant and inventor</p> <p><input type="checkbox"/> inventor only <i>(If this check-box is marked, do not fill in below.)</i></p>	
<p><b>State (that is, country) of nationality:</b> France (FR)</p>		<p><b>State (that is, country) of residence:</b> France (FR)</p>	
<p><b>This person is applicant for the purposes of:</b></p> <p><input type="checkbox"/> all designated States    <input type="checkbox"/> all designated States except the United States of America    <input checked="" type="checkbox"/> the United States of America only    <input type="checkbox"/> the States indicated in the Supplemental Box</p>			
<p><input checked="" type="checkbox"/> Further applicants and/or (further) inventors are indicated on another continuation sheet.</p>			

**Box No.V DESIGNATION OF STATES**

The following designations are hereby made under Rule 4.9(a) (mark the applicable check-box; at least one must be marked):

**Regional Patent**

- ☐ **AP** ARIPO Patent: GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, SD Sudan, SL Sierra Leone, SZ Swaziland, UG Uganda, ZW Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT
- ☐ **EA** Eurasian Patent: AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
- ☒ **EP** European Patent: AT Austria, BE Belgium, CH and LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- ☐ **OA** OAPI Patent: BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Côte d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, GW Guinea-Bissau, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT (if other kind of protection or treatment desired, specify on dotted line) .....

**National Patent** (if other kind of protection or treatment desired, specify on dotted line):

- |                                                                                |                                                                              |
|--------------------------------------------------------------------------------|------------------------------------------------------------------------------|
| <input type="checkbox"/> <b>AE</b> United Arab Emirates                        | <input type="checkbox"/> <b>LR</b> Liberia                                   |
| <input type="checkbox"/> <b>AL</b> Albania                                     | <input type="checkbox"/> <b>LS</b> Lesotho                                   |
| <input type="checkbox"/> <b>AM</b> Armenia                                     | <input type="checkbox"/> <b>LT</b> Lithuania                                 |
| <input type="checkbox"/> <b>AT</b> Austria                                     | <input type="checkbox"/> <b>LU</b> Luxembourg                                |
| <input type="checkbox"/> <b>AU</b> Australia                                   | <input type="checkbox"/> <b>LV</b> Latvia                                    |
| <input type="checkbox"/> <b>AZ</b> Azerbaijan                                  | <input type="checkbox"/> <b>MD</b> Republic of Moldova                       |
| <input type="checkbox"/> <b>BA</b> Bosnia and Herzegovina                      | <input type="checkbox"/> <b>MG</b> Madagascar                                |
| <input type="checkbox"/> <b>BB</b> Barbados                                    | <input type="checkbox"/> <b>MK</b> The former Yugoslav Republic of Macedonia |
| <input type="checkbox"/> <b>BG</b> Bulgaria                                    |                                                                              |
| <input type="checkbox"/> <b>BR</b> Brazil                                      | <input type="checkbox"/> <b>MN</b> Mongolia                                  |
| <input type="checkbox"/> <b>BY</b> Belarus                                     | <input type="checkbox"/> <b>MW</b> Malawi                                    |
| <input checked="" type="checkbox"/> <b>CA</b> Canada                           | <input type="checkbox"/> <b>MX</b> Mexico                                    |
| <input type="checkbox"/> <b>CH</b> and <b>LI</b> Switzerland and Liechtenstein | <input type="checkbox"/> <b>NO</b> Norway                                    |
| <input type="checkbox"/> <b>CN</b> China                                       | <input type="checkbox"/> <b>NZ</b> New Zealand                               |
| <input type="checkbox"/> <b>CU</b> Cuba                                        | <input type="checkbox"/> <b>PL</b> Poland                                    |
| <input type="checkbox"/> <b>CZ</b> Czech Republic                              | <input type="checkbox"/> <b>PT</b> Portugal                                  |
| <input type="checkbox"/> <b>DE</b> Germany                                     | <input type="checkbox"/> <b>RO</b> Romania                                   |
| <input type="checkbox"/> <b>DK</b> Denmark                                     | <input type="checkbox"/> <b>RU</b> Russian Federation                        |
| <input type="checkbox"/> <b>EE</b> Estonia                                     | <input type="checkbox"/> <b>SD</b> Sudan                                     |
| <input type="checkbox"/> <b>ES</b> Spain                                       | <input type="checkbox"/> <b>SE</b> Sweden                                    |
| <input type="checkbox"/> <b>FI</b> Finland                                     | <input type="checkbox"/> <b>SG</b> Singapore                                 |
| <input type="checkbox"/> <b>GB</b> United Kingdom                              | <input type="checkbox"/> <b>SI</b> Slovenia                                  |
| <input type="checkbox"/> <b>GD</b> Grenada                                     | <input type="checkbox"/> <b>SK</b> Slovakia                                  |
| <input type="checkbox"/> <b>GE</b> Georgia                                     | <input type="checkbox"/> <b>SL</b> Sierra Leone                              |
| <input type="checkbox"/> <b>GH</b> Ghana                                       | <input type="checkbox"/> <b>TJ</b> Tajikistan                                |
| <input type="checkbox"/> <b>GM</b> Gambia                                      | <input type="checkbox"/> <b>TM</b> Turkmenistan                              |
| <input type="checkbox"/> <b>HR</b> Croatia                                     | <input type="checkbox"/> <b>TR</b> Turkey                                    |
| <input type="checkbox"/> <b>HU</b> Hungary                                     | <input type="checkbox"/> <b>TT</b> Trinidad and Tobago                       |
| <input type="checkbox"/> <b>ID</b> Indonesia                                   | <input type="checkbox"/> <b>UA</b> Ukraine                                   |
| <input type="checkbox"/> <b>IL</b> Israel                                      | <input type="checkbox"/> <b>UG</b> Uganda                                    |
| <input type="checkbox"/> <b>IN</b> India                                       | <input checked="" type="checkbox"/> <b>US</b> United States of America       |
| <input type="checkbox"/> <b>IS</b> Iceland                                     |                                                                              |
| <input checked="" type="checkbox"/> <b>JP</b> Japan                            | <input type="checkbox"/> <b>UZ</b> Uzbekistan                                |
| <input type="checkbox"/> <b>KE</b> Kenya                                       | <input type="checkbox"/> <b>VN</b> Viet Nam                                  |
| <input type="checkbox"/> <b>KG</b> Kyrgyzstan                                  | <input type="checkbox"/> <b>YU</b> Yugoslavia                                |
| <input type="checkbox"/> <b>KP</b> Democratic People's Republic of Korea       | <input type="checkbox"/> <b>ZA</b> South Africa                              |
|                                                                                | <input type="checkbox"/> <b>ZW</b> Zimbabwe                                  |

Check-boxes reserved for designating States which have become party to the PCT after issuance of this sheet:

- |                                               |                                             |
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| <input type="checkbox"/> <b>CR</b> COSTA RICA | <input type="checkbox"/> <b>TZ</b> TANZANIA |
| <input type="checkbox"/> <b>DM</b> DOMINICA   | <input type="checkbox"/> <b>MA</b> MOROCCO  |

**Precautionary Designation Statement:** In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (Confirmation of a designation consists of the filing of a notice specifying that designation and the payment of the designation and confirmation fees. Confirmation must reach the receiving Office within the 15-month time limit.)



## Box No. VI PRIORITY CLAIM

☐ Further priority claims are indicated in the Supplemental Box.

Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country	regional application: * regional Office	international application: receiving Office
item (1) (08.10.99) October 8, 1998	1010269	The Netherlands		
item (2)				
item (3)				

☒ The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of the present international application is the receiving Office) identified above as item(s): 1

\* Where the earlier application is an ARIPO application, it is mandatory to indicate in the Supplemental Box at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed (Rule 4.10(b)(ii)). See Supplemental Box.

## Box No. VII INTERNATIONAL SEARCHING AUTHORITY

Choice of International Searching Authority (ISA)  
(if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):

ISA / EPA

Request to use results of earlier search; reference to that search (if an earlier search has been carried out by or requested from the International Searching Authority):

Date (day/month/year)

Number

Country (or regional Office)

June 15, 1999

SN 31955 NL

The Netherlands

## Box No. VIII CHECK LIST; LANGUAGE OF FILING

This international application contains the following number of sheets:

request : 4

description (excluding sequence listing part) : 4

claims : 1

abstract : 1

drawings : 2

sequence listing part of description :

Total number of sheets : 12

This international application is accompanied by the item(s) marked below:

- ☒ fee calculation sheet
- ☐ separate signed power of attorney
- ☐ copy of general power of attorney; reference number, if any:
- ☐ statement explaining lack of signature
- ☐ priority document(s) identified in Box No. VI as item(s):
- ☐ translation of international application into (language):
- ☐ separate indications concerning deposited microorganism or other biological material
- ☐ nucleotide and/or amino acid sequence listing in computer readable form
- ☒ other (specify): copy search report

Figure of the drawings which should accompany the abstract:

Language of filing of the international application:

English

## Box No. IX SIGNATURE OF APPLICANT OR AGENT

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).

JORRITSMA, R.

7 October 1999

Nederlandsch Octrooibureau, The Hague,

For receiving Office use only

1. Date of actual receipt of the purported international application: 08 OCT (08.10.99)	2. Drawings: <input checked="" type="checkbox"/> received: <input type="checkbox"/> not received:
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:	
4. Date of timely receipt of the required corrections under PCT Article 11(2):	
5. International Searching Authority (if two or more are competent): ISA /	6. <input type="checkbox"/> Transmittal of search copy delayed until search fee is paid.

For International Bureau use only

Date of receipt of the record copy by the International Bureau:

02 NOVEMBER 1999

(02.11.99)

Werkwijze voor het bekleden van een dragerplaat  
en brandstofcel voorzien van een dergelijke dragerplaat.

De onderhavige uitvinding heeft betrekking op een werkwijze voor het bekleden  
5 van een niet-geoxideerde roestvast stalen dragerplaat met een elektrisch geleidende  
corrosiewerende bekleding, omvattende het opbrengen van een diffusieafsluitlaag met  
een titaanverbinding, gevolgd door het aanbrengen van een nikkellaag. Een dergelijke  
werkwijze toegepast in een brandstofcel is bekend uit het Duitse Offenlegungsschrift  
19523637. Aan het zich aan de anodezijde bevindende deel van de brandstofcel worden  
10 hoge eisen gesteld. Enerzijds moet dit in staat zijn de via de anode-zijdige  
gasverdeelinrichting toegevoerde stroom af te voeren. Anderzijds moet dit voldoende  
corrosiebestendig zijn om aan de thans gestelde eisen van levensduur te voldoen. Op dit  
moment is een levensduur van enkele tienduizenden uren vereist. Door het agressieve  
milieu resulterende uit carbonaatmateriaal, hoge temperatuur en de verhoudingsgewijs  
15 lage potentiaal aan de anode, wordt deze zijde van de separatorplaat bijzonder zwaar  
belast.

Om de corrosieproblemen te vermijden wordt in het bovengenoemde Duitse  
Offenlegungsschrift voorgesteld om op de roestvast stalen separatorplaat aan de  
anodezijde een bekleding aan te brengen bestaande uit een titaannitridelaag waarop een  
20 nikkellaag aangebracht is. Deze nikkellaag voorziet in bescherming, maar voorkomen  
dient te worden dat het basismateriaal uit het RVS in het nikkel diffundeert. Immers  
waargenomen is dat de sterkte van de resterende nikkellaag door een dergelijk  
diffusieproces aanzienlijk afneemt en binnen 10.000 uur de resterende nikkellaag  
losbreekt van de RVS-laag en de cel snel niet werkzaam wordt. De dikte van de  
25 titaannitridelaag ligt volgens het Duitse Offenlegungsschrift 19523637 bij voorkeur  
tussen 0,5 en 5  $\mu\text{m}$ . Verondersteld wordt dat door contact met het carbonaatmateriaal  
het titaannitride omgezet wordt naar titaanoxide. Gebleken is echter dat dit oxide een  
groter volume heeft en daardoor plaatselijk de nikkellaag wegdrukt. Bovendien is  
gebleken dat een zo verkregen titaanoxidelaag niet dicht is en aantasting van het  
30 basismateriaal daardoor niet voorkomen kan worden.

In het Duitse Offenlegungsschrift 4030943 wordt een anode beschreven  
opgebouwd uit poreus nikkel en titaanoxide. Bij contact met lithiumcarbonaat ontstaat  
lithiumtitanaat, hetgeen de bevochtiging van de poreuze nikkel anode bevordert doordat

carbonaatmateriaal gemakkelijker de anode binnendringt. De separatorplaat of bipolaire plaat is vernikkeld en bestaat uit RVS-materiaal.

Het doel van de onderhavige uitvinding is in een werkwijze te voorzien voor het bekleden van een separatorplaat van een brandstofcel waarbij een diffusieafsluitlaag  
5 toegepast wordt die ook na langer bedrijf in stand blijft en waarbij de daarop liggende corrosiewerende nikkellaag niet beïnvloed wordt.

Dit doel wordt bij een hierboven beschreven werkwijze verwezenlijkt doordat die titaanverbinding titaanoxide omvat.

Door direct titaanoxide op het RVS-basismateriaal aan te brengen, vindt bij het  
10 diffunderen van carbonaat door de poreuze nikkelbovenlaag geen schadelijke reactie plaats. Verondersteld wordt dat  $\text{TiO}_2$  in contact met het carbonaat de toplaag omgezet wordt in  $\text{Li}_2\text{TiO}_3$ . Dit heeft geen negatief effect op de elektrische eigenschappen van de coating. De bulk van het  $\text{TiO}_2$  wordt omgezet in een natrium-titanium brons of een kalium-titanium brons. Dit materiaal heeft nog steeds afsluitende eigenschappen ten  
15 opzichte van de legeringselementen uit het RVS. Verdere garantie dat de barrièrelaag ook gedurende langere tijd in stand blijft, wordt verwezenlijkt door deze laag een aanzienlijke dikte te geven. Bij voorkeur is deze dikte ten minste 25  $\mu\text{m}$  en meer in het bijzonder ligt deze tussen 40 en 50  $\mu\text{m}$ .

De hierboven beschreven titaanoxidelaag kan op alle in de stand der techniek  
20 bekende wijzen aangebracht worden. Voorbeelden zijn onder atmosferische druk aanbrengen van een plasmaversproeiing, of high velocity oxygen flame versproeiing, sputteren, verdampen met een boog, met een boog hechten en sputteren, ionenplatteren of CVD.

Volgens een verdere van voordeel zijnde uitvoering van de uitvinding wordt het  
25 titaanoxide pas op de RVS-drager aangebracht nadat daarop een hechtlaag is geplaatst, zoals van  $\text{NiCrAlY}$ .

Zoals hierboven beschreven, heeft de uitvinding in het bijzonder toepassing voor een brandstofcel waarbij de separatorplaat of bipolaire plaat aan de anodezijde behandeld is zoals hierboven beschreven. Begrepen dient te worden dat in andere  
30 toepassingen in agressieve omstandigheden waarbij elektrische geleiding vereist is, de hierboven beschreven werkwijze gebruikt kan worden. De uitvinding kan bij elk soort electrochemische cel en meer in het bijzonder brandstofcel gebruikt worden zoals MCFC-cellen en SOFC-cellen.

De uitvinding zal hieronder aan de hand van een in de tekening afgebeeld uitvoeringsvoorbeeld verduidelijkt worden, waarbij de verschillende delen niet op dezelfde schaal weergegeven zijn. Daarbij toont:

Fig. 1 schematisch in dwarsdoorsnede een deel van een MCFC-cel nabij de separatorplaat volgens de uitvinding;

Fig. 2 in detail in dwarsdoorsnede een deel van een separatorplaat gericht naar de anode, en

Fig. 3 grafisch de celspanning van een cel volgens de uitvinding.

In fig. 1 is een deel van een MCFC-cel getoond voorzien van een separatorplaat 7 waarop een anode-zijdige gasverdeelinrichting 4 aansluit waartegen stroomcollector 8 ligt waarop een anode 5 aansluit. Zowel de anode als de corrugatie kunnen uit nikkelmateriaal bestaan. De anode bestaat meer in het bijzonder uit nikkel met 10 gew.% Cr.

In fig. 2 is de separatorplaat 7 in detail afgebeeld. Deze bestaat uit een drager van RVS materiaal, zoals 3 AISI 310 met een dikte van bijvoorbeeld 0,5 mm. Daarop is een hechtlaag 6 aangebracht van een metaalchroomaluminiumyttriumlegering zoals NiCrAlY. De dikte daarvan is ongeveer 40-60  $\mu\text{m}$ . Dit hechtlaagmateriaal kan in poedervormige toestand opgebracht worden door uit te gaan van een NiCrAlY poeder met een deeltjesgrootte tussen 10 en 45  $\mu\text{m}$  wat met HVOF spuittechniek opgebracht wordt.

Een dergelijke hechtlaag wordt aangebracht om voor verschil in uitzettingscoëfficiënt tussen roestvast staal en de titaanoxidelaag te compenseren. Alvorens een dergelijke hechtlaag aan te brengen op het roestvast stalen dragermateriaal kan dit roestvast staalmateriaal opgeruwd worden met enige in de stand der techniek bekende wijze. Bijvoorbeeld vindt opruwen plaats door middel van gritten met AL<sub>2</sub>O<sub>3</sub> gritpoeder.

Vervolgens is met de high velocity oxygen flame sproeitechniek daarop een titaanoxidelaag aangebracht met een dikte liggend tussen 40 en 50  $\mu\text{m}$ . Deze laag is met 2 aangegeven. Daarbij wordt uitgegaan van een poeder met een deeltjesgrootte tussen 5 en 20  $\mu\text{m}$ . Dit poeder kan eventueel gedoteerd worden met een vijfwaardig ion in het bijzonder met niobium of tantaal. Aan niobium wordt de meeste voorkeur gegeven. De porositeit van de titaanoxidelaag is typisch 2%. Daarop is een nikkellaag 3 aangebracht op enige in de stand der techniek bekende wijze met een dikte die

eveneens tussen 25 en 50  $\mu\text{m}$  ligt. Ook hier wordt bij voorkeur HVOF-sputtechniek toegepast.

5 Bij proeven onder corrosieve omstandigheden met de potentiaal aangelegd op de anode zoals deze in gebruik te verwachten valt, is na 3.000 uur geen wezenlijke aantasting van het RVS basismateriaal waargenomen bij een temperatuur van ongeveer 650°C. Op grond hiervan kan worden geëxtrapoleerd dat een levensduur groter dan 40.000 uur haalbaar is.

10 In fig. 3 is de celspanning van een 100  $\text{cm}^2$  cel met een coating volgens de uitvinding onder gesimuleerde systeemcondities weergegeven. De celspanning (650 mV) is vergelijkbaar met standaardcellen onder gesimuleerde systeemcondities waardoor het effect van de uitvinding blijkt.

15 Hoewel de uitvinding hierboven aan de hand van een voorkeursuitvoering beschreven is, dient begrepen te worden dat daaraan wijzigingen aangebracht kunnen worden die voor degenen bekwaam in de stand der techniek direct voor de hand liggend zijn na het lezen van bovenstaande beschrijving en liggen binnen het bereik van de bijgevoegde conclusies.

## Conclusies

1. Werkwijze voor het bekleden van een niet-geoxideerde roestvast stalen dragerplaat met een elektrisch geleidende corrosiewerende bekleding, omvattende het opbrengen van een diffusieafsluitlaag met een titaanverbinding, gevolgd door het  
5 aanbrengen van een nikkellaag, met het kenmerk, dat die titaanverbinding titaanoxide omvat.

2. Werkwijze volgens conclusie 1, waarbij ten minste een van die opgebrachte lagen een dikte van ten minste 25  $\mu\text{m}$  heeft.

3. Werkwijze volgens een van de voorgaande conclusies, waarbij voor het  
10 opbrengen van titaanoxide een hechtlaag op de dragerplaat aangebracht wordt.

4. Werkwijze volgens conclusie 3, waarbij die hechtlaag NiCrAlY omvat.

5. Werkwijze volgens een van de voorgaande conclusies, waarbij ten minste een van die lagen door High Velocity Oxygen Flame sproeien opgebracht wordt.

6. Brandstofcelstapel omvattende een aantal cellen met elk een kathode, anode  
15 en elektrolyt, waarbij die cellen gescheiden zijn door een separatorplaat, waarbij die separatorplaat een dragerplaat uit roestvast staal omvat aan de anodezijde bekleed met een diffusieafsluitlaag omvattende titaanoxide voorzien van een nikkellaag.

7. Brandstofcelstapel volgens conclusie 6, waarbij die titaanoxidelaag en/of nikkellaag een dikte van ten minste 25  $\mu\text{m}$  heeft.

20 8. Brandstofcelstapel volgens conclusie 6 of 7, waarbij tussen die roestvast stalen dragerplaat en die titaanoxidelaag een hechtlaag aangebracht is.

9. Brandstofcelstapel volgens conclusie 8, waarbij die hechtlaag NiCrAlY omvat.

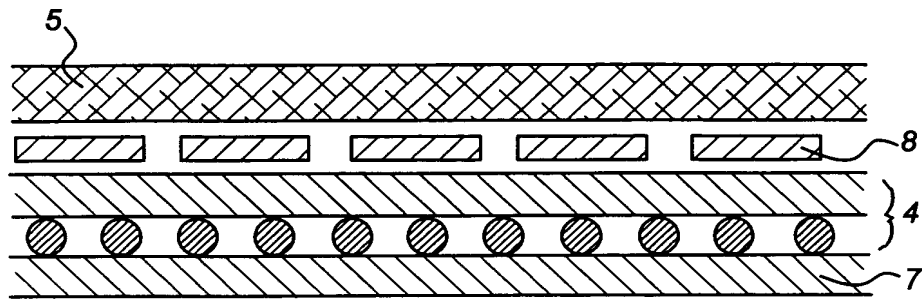
25 10. Brandstofcelstapel volgens een van de conclusies 6-9 waarbij de brandstofcelstapel carbonaatbrandstofcellen omvat.

\*\*\*\*\*

## Uittreksel

Werkwijze voor het bekleden van een niet-geoxideerde RVS-dragerplaat alsmede MCFC-brandstofcelstapel voorzien van een zo beklede separatorplaat. Aan de  
5 anodezijde van deze dragerplaat wordt eerst een diffusieafsluitlaag gevolgd door een nikkellaag aangebracht. Deze diffusieafsluitlaag bestaat uit titaanoxide en de hechting tussen titaanoxide en de dragerplaat kan verbeterd worden door het voorzien in een hechtlaag.

*Fig 1*



*Fig 2*

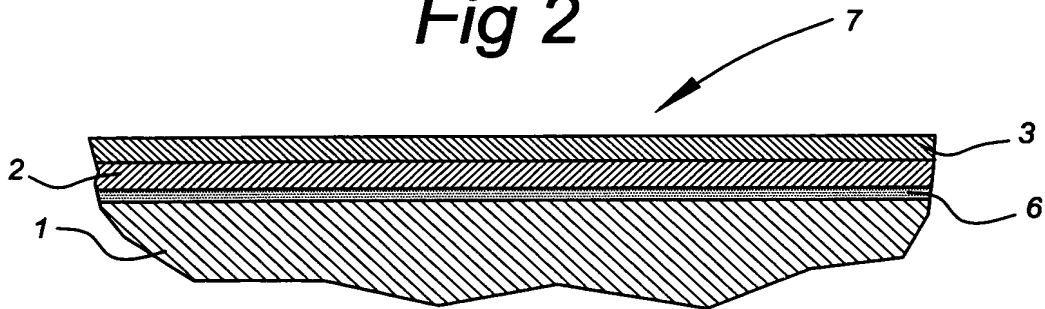
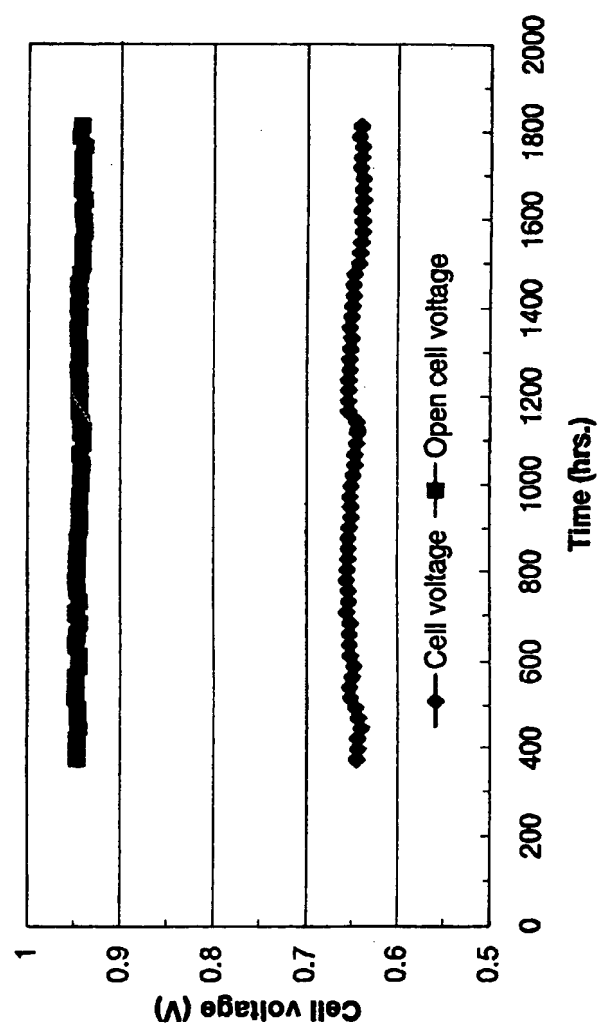




Fig 3



PATENT COOPERATION TREATY

Nederlandsch Octrooibureau  
INGEK. 20 APR 2000  
PCT  
Paraaf Boverken

From the INTERNATIONAL BUREAU

To:  
DE BRUIJN, Leendert, C.  
Nederlandsch Octrooibureau  
Scheveningseweg 82  
P.O. Box 29720  
NL-2502 LS The Hague  
PAYS-BAS

**NOTICE INFORMING THE APPLICANT OF THE  
COMMUNICATION OF THE INTERNATIONAL  
APPLICATION TO THE DESIGNATED OFFICES**

(PCT Rule 47.1(c), first sentence)

Date of mailing (day/month/year) 13 April 2000 (13.04.00)		<b>IMPORTANT NOTICE</b>	
Applicant's or agent's file reference BO 41866			
International application No. PCT/NL99/00624	International filing date (day/month/year) 08 October 1999 (08.10.99)	Priority date (day/month/year) 08 October 1998 (08.10.98)	
Applicant STICHTING ENERGIEONDERZOEK CENTRUM NEDERLAND et al			

1. Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this Notice:  
JP,US

In accordance with Rule 47.1(c), third sentence, those Offices will accept the present Notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:  
CA,EP

The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-bis)).

3. Enclosed with this Notice is a copy of the international application as published by the International Bureau on  
13 April 2000 (13.04.00) under No. WO 00/21152

**REMINDER REGARDING CHAPTER II (Article 31(2)(a) and Rule 54.2)**

If the applicant wishes to postpone entry into the national phase until 30 months (or later in some Offices) from the priority date, a **demand for international preliminary examination** must be filed with the competent International Preliminary Examining Authority before the expiration of 19 months from the priority date.

It is the applicant's sole responsibility to monitor the 19-month time limit.

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

**REMINDER REGARDING ENTRY INTO THE NATIONAL PHASE (Article 22 or 39(1))**

If the applicant wishes to proceed with the international application in the **national phase**, he must, within 20 months or 30 months, or later in some Offices, perform the acts referred to therein before each designated or elected Office.

For further important information on the time limits and acts to be performed for entering the national phase, see the Annex to Form PCT/IB/301 (Notification of Receipt of Record Copy) and Volume II of the PCT Applicant's Guide.

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<b>(54) Title:</b> METHOD FOR COATING A SUPPORT PLATE AND FUEL CELL PROVIDED WITH SUCH A SUPPORT PLATE		
<b>(57) Abstract</b>		
<p>Method for coating a non-oxidised stainless steel support plate and a MCFC fuel cell stack provided with a separator plate coated in this way. First a diffusion barrier layer and then a nickel layer are applied to the anode side of said support plate. Said diffusion barrier layer consists of titanium oxide and the adhesion between titanium oxide and the support plate can be improved by providing an adhesion layer.</p>		

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Method for coating a support plate  
and fuel cell provided with such a support plate

— The present invention relates to a method for coating a non-oxidised stainless steel support plate with an electrically conducting corrosion-resistant coating, comprising applying a diffusion barrier layer containing a titanium compound, followed by applying a nickel layer. A method of this type is disclosed in German Offenlegungsschrift 19523637. High demands are imposed on that part of the fuel cell which is located on the anode side. On the one hand this must be capable of discharging the stream supplied via the gas distribution device on the anode side. On the other hand this must be sufficiently corrosion-resistant to meet current requirements in respect of service life. Currently a service life of a few ten thousand hours is required. Because of the aggressive environment resulting from carbonate material, high temperature and the relatively low potential at the anode, this side of the separator plate is particularly severely stressed.

In order to avoid the corrosion problems it is proposed in the abovementioned German Offenlegungsschrift to apply a coating, consisting of a titanium nitride layer on top of which a nickel layer has been applied, on the anode side of the stainless steel separator plate. This nickel layer provides protection but the base material from the stainless steel must be prevented from diffusing into the nickel. After all, it has been observed that the strength of the residual nickel layer decreases appreciably as a result of such a diffusion process and within 10 000 hours the residual nickel layer detaches from the stainless steel layer and the cell rapidly becomes inoperative. According to German Offenlegungsschrift 19523637, the thickness of the titanium nitride layer is preferably between 0.5 and 5  $\mu\text{m}$ . It is assumed that the titanium nitride is converted to titanium oxide by contact with the carbonate material. However, it has been found that this oxide has a larger volume and consequently locally pushes away the nickel layer. Moreover, it has been found that a titanium oxide layer obtained in this way is not impermeable and attack on the base material can consequently not be prevented.

In German Offenlegungsschrift 4030943 an anode made up of porous nickel and titanium oxide is described. On contact with lithium carbonate lithium titanate is produced, which promotes moistening of the porous nickel anode because carbonate material penetrates into the anode more easily. The separator plate or bipolar plate is nickel-coated and consists of stainless steel material.

The aim of the present invention is to provide a method for coating a separator plate of a fuel cell wherein a diffusion barrier layer is used which remains intact even after prolonged operation and wherein the corrosion-resistant nickel layer arranged thereon is not affected.

This aim is achieved with a method as described above in that said titanium compound  
5 comprises titanium oxide.

As a result of applying titanium oxide directly to the stainless steel base material, no harmful reaction takes place when carbonate diffuses through the porous nickel top layer. It is assumed that  $\text{TiO}_2$  in contact with the carbonate converts the top layer into  $\text{Li}_2\text{TiO}_3$ . This does not have any adverse effect on the electrical properties of the coating. The bulk of the  
10  $\text{TiO}_2$  is converted into a sodium-titanium bronze or a potassium-titanium bronze. This material still has barrier properties relative to the alloy elements from the stainless steel. A further guarantee that the barrier layer remains intact even during a prolonged period is achieved by giving the layer an appreciable thickness. Preferably the thickness is at least 25  $\mu\text{m}$  and more particularly is between 40 and 50  $\mu\text{m}$ .

15 The titanium oxide layer described above can be applied in any way known from the prior art. Examples are application of a plasma spray under atmospheric pressure or high velocity oxygen flame spraying, sputtering, vaporisation using an arc, adhesion and sputtering using an arc, ion plating or CVD.

According to a further advantageous embodiment of the invention the titanium oxide is  
20 applied to the stainless steel support only after an adhesion layer, such as a layer of  $\text{NiCrAlY}$ , has been placed thereon.

As described above, the invention is used in particular for a fuel cell in which the separator plate or bipolar plate on the anode side has been treated as described above. It must be understood that the method described above can be used in other applications under  
25 aggressive conditions where electrical conduction is required.

The invention will be explained below with reference to an illustrative embodiment shown in the drawing, in which the various components are not shown on the same scale. In the drawing:

Fig. 1 shows, diagrammatically in cross-section, part of an MCFC cell close to the  
30 separator plate according to the invention; and

Fig. 2 shows, in detail in cross-section, part of a separator plate facing the anode.

Fig. 1 shows part of an MCFC cell provided with a separator plate 7 which is adjoined

by a gas distribution device 4 on the anode side, with which current collector 8 is in contact, which is adjoined by an anode 5. Both the anode and the corrugation can be made of nickel material. The anode consists more particularly of nickel containing 10 % (by wt.) Cr.

The separator plate 7 is shown in detail in Fig. 2. This separator plate consists of a support of stainless steel material, such as 3 AISI 310 having a thickness of, for example, 0.5 mm. An adhesion layer 6 composed of a metal chromium aluminium yttrium alloy, such as NiCrAlY, is applied on top of this. The thickness of this layer is approximately 40-60  $\mu\text{m}$ . The adhesion layer material can be applied in powder form by using as the starting material an NiCrAlY powder having a particle size of between 10 and 45  $\mu\text{m}$ , which is applied using the HVOF spraying technique.

An adhesion layer of this type is applied in order to compensate for the difference in the coefficient of expansion between stainless steel and the titanium oxide layer. Before applying such an adhesion layer to the stainless steel support material, the stainless steel material can be roughened by any method known from the prior art. For example roughening takes place by means of grit blasting with fine  $\text{Al}_2\text{O}_3$  grit.

A titanium oxide layer having a thickness of between 40 and 50  $\mu\text{m}$  is then applied thereon using the high velocity oxygen flame spraying technique. This layer is indicated by 2. The starting material used for this layer is a powder having a particle size of between 5 and 20  $\mu\text{m}$ . This powder can optionally be doped with a pentavalent ion, in particular with niobium or tantalum. Niobium is the most preferred. The porosity of the titanium oxide layer is typically 2 %. A nickel layer 3, having a thickness which is likewise between 25 and 50  $\mu\text{m}$ , is applied on top of said titanium oxide layer by any method known from the prior art. In this case also the HVOF spraying technique is preferably used.

In tests under corrosive conditions with the potential applied to the anode, as is to be expected in use, no substantial attack on the stainless steel base material was detected at a temperature of approximately 650 °C after 3 000 hours. On the basis of this it can be extrapolated that a service life of more than 40 000 hours is achievable.

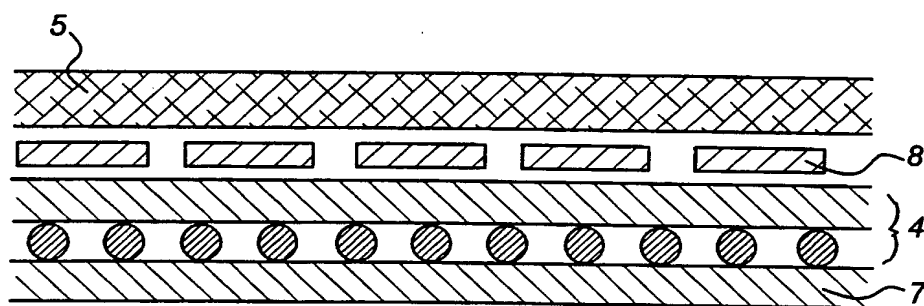
Although the invention has been described above with reference to a preferred embodiment, it must be understood that modifications can be made thereto which are immediately obvious to those skilled in the art after reading the above description and are within the scope of the appended claims.

**Claims**

1. Method for coating a non-oxidised stainless steel support plate with an electrically conducting corrosion-resistant coating, comprising applying a diffusion barrier layer containing a titanium compound, followed by applying a nickel layer, characterised in that said titanium compound comprises titanium oxide.
2. Method according to Claim 1, wherein at least one of said applied layers has a thickness of at least 25  $\mu\text{m}$ .
3. Method according to one of the preceding claims, wherein an adhesion layer is applied to the support plate before titanium oxide is applied.
4. Method according to Claim 3, wherein said adhesion layer comprises NiCrAlY.
5. Method according to one of the preceding claims, wherein at least one of said layers is applied by high velocity oxygen flame spraying.
6. Fuel cell stack comprising a number of cells each having a cathode, anode and electrolyte, wherein said cells are separated by a separator plate, said separator plate comprising a support plate of stainless steel coated on the anode side with a diffusion barrier layer comprising titanium oxide provided with a nickel layer.
7. Fuel cell according to Claim 6, wherein said titanium oxide layer and/or nickel layer has a thickness of at least 25  $\mu\text{m}$ .
8. Fuel cell according to Claim 6 or 7, wherein an adhesion layer is applied between said stainless steel support plate and said titanium oxide layer.
9. Fuel cell according to Claim 8, wherein said adhesion layer comprises NiCrAlY.



*Fig 1*



*Fig 2*

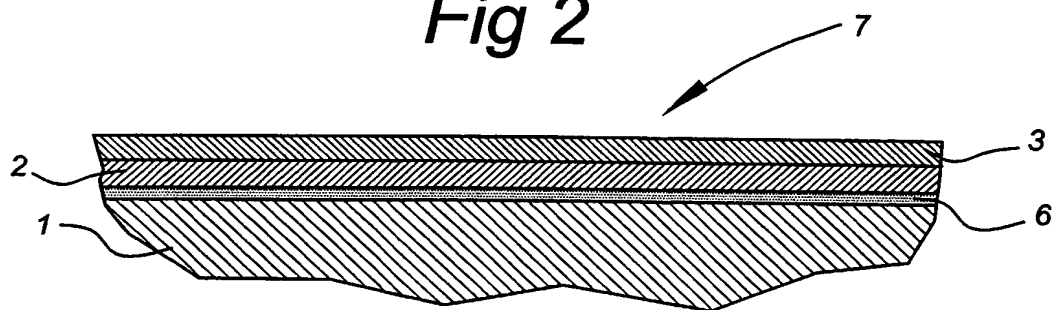


Fig 3

